

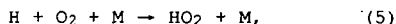
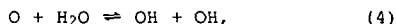
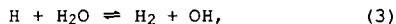
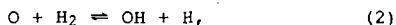
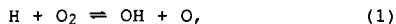
THERMAL RATE CONSTANT MEASUREMENTS BY THE
FLASH OR LASER PHOTOLYSIS-SHOCK TUBE METHOD:
RESULTS FOR THE OXIDATIONS OF H₂ AND D₂

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INTRODUCTION

This article discusses the FP- or LP-ST technique. The modeling of the oxidation of H₂ will be specifically featured. The reactions that pertain to this oxidative system and that have been studied by either the FP- or LP-ST technique, will be reviewed. These include,



and their deuterated modifications. Both forward and reverse processes will be included in the discussion since, in all cases, the existing data indicate that the reactions are microscopically reversible. Hence, data evaluations can be made over very large temperature ranges.

EXPERIMENTAL

The FP-ST technique was first suggested by Burns and Hornig¹ and was followed by some OH-radical reaction studies by Zellner and coworkers.² The technique has recently been extended with the atomic resonance absorption spectroscopic (ARAS) method of detection.³ This extension naturally follows from the earlier work.^{1,2} A less ambiguous experiment is now possible since spectroscopic absorption by atomic species is stronger than by diatomic or polyatomic radicals, and thus, smaller concentrations can be detected thereby eliminating complications from secondary reactions. This development has allowed absolute bimolecular rate constants to be directly studied over a large T-range, ~650 to 2500 K.

The shock tube methods that are used in FP- or LP-ST studies are traditional.⁴ A schematic diagram of a recently constructed apparatus⁵ is shown in Fig. 1. The technique has been described previously,^{5,6,7} and therefore, only a brief description will be given here. The method utilizes the double heating effect that can be obtained by reflected shock wave methods. The nearly stagnant gas in the reflected shock wave regime is subjected to either flash or laser photolysis thereby producing an atomic species in the central hot gas region. The time dependence of the atomic species is then radially monitored as it reacts with an added reactant molecule. It is

necessary to have a source molecule present which, on photolysis, gives the atomic species of interest.

If the transmittance for any atomic absorption experiment can be held above ~0.8, then Beer's law will hold to a good approximation if the line is not too highly reversed. In FP- and LP-ST experiments with unreversed or only partially reversed resonance lamps, it is therefore only necessary to measure the temporal behavior of absorbance, (ABS), where $(ABS) \equiv -\ln(I/I_0)$. Since Beer's law holds, the atom concentration, [A], is equal to $(ABS)/\sigma_A l$. In all cases, the reactant concentration is very much larger than that of the atom, and therefore, the decay of A will obey pseudo-first-order kinetics. Since [A] is proportional to (ABS), it is only necessary to measure the temporal behavior of absorbance, $(ABS)_t$, in a kinetics experiment. The rate of depletion of the atomic species is the product of the thermal rate constant times the concentrations of the reactant and the depleting atomic concentration. After integration, a plot of $\ln(ABS)_t$ against time will yield a decay constant that is equal to the product of the thermal rate constant times the reactant concentration. Fig. 2 shows a typical plot of an experiment. The top panel shows an actual raw data signal and the bottom panel shows the first-order plot derived from the top panel. The negative slope of the plot gives the decay constant which, on division by the reactant concentration, gives a measurement of the thermal rate constant at the conditions of the experiment as determined from the initial pressure, temperature, and the shock strength.

RESULTS

$H + O_2 \rightarrow OH + O$ and $D + O_2 \rightarrow OD + O$: The first published LP-ST paper⁸ showed that the photolysis of H_2O at 193 nm yields both H-atoms and OH-radicals at high temperatures. In recent LP-ST experiments,⁹ H_2O photolyte was used at $T \approx 1085$ K. With the higher fluences from excimer laser photolysis, experiments could be performed with less H_2O being present than in an earlier FP-ST study that used the same technique of detection.¹⁰ This has allowed experiments to be performed at substantially higher T, up to 2278 K. Fig. 2 shows a typical experiment. Data with both H_2O and NH_3 as photolyte molecules have yielded the Arrhenius result,

$$k_1 = (1.15 \pm 0.16) \times 10^{-10} \exp(-6917 \pm 193 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (6)$$

for $1103 \leq T \leq 2055$ K. Similar results for reaction (1D) with D_2O as photolyte give the Arrhenius result,

$$k_{1D} = (1.09 \pm 0.20) \times 10^{-10} \exp(-6937 \pm 247 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (7)$$

for $1085 \leq T \leq 2278$ K. The reverse rate constants can be determined from JANAF equilibrium values,¹¹ and rate constants for forward and reverse processes are listed in Table I.

$O + H_2 \rightarrow OH + H$ and $O + D_2 \rightarrow OD + H$: FP-ST experiments with NO as the O-atom source have been carried out on both the H_2 ¹² and D_2 ⁵ reactions. The results for $O + H_2$ can be described by the Arrhenius equation,

$$k_2 = (3.10 \pm 0.20) \times 10^{-10} \exp(-6854 \pm 84 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (8)$$

for $880 \leq T \leq 2495$ K. $O + D_2$ can similarly be described by,

$$k_{2D} = (3.22 \pm 0.25) \times 10^{-10} \exp(-7293 \pm 98 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (9)$$

for $825 \leq T \leq 2487$ K. Earlier shock tube determinations are in reasonable agreement with these direct results. There are also a number of lower temperature determinations for k_{212-16} and $k_{2D14-18}$. The most reliable low T data are those of Sutherland et al.,¹² Westenberg and deHaas,^{13,17} Presser and Gordon,¹⁶ and Zhu et al.¹⁸ These data have been combined with the FP-ST data to give three parameter expressions that can be used over the entire experimental temperature range.

$$k_2 = 8.44 \times 10^{-20} T^{2.67} \exp(-3167 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (10)$$

for $297 \leq T \leq 2495$ K,¹² and,

$$k_{2D} = 2.43 \times 10^{-16} T^{1.70} \exp(-4911 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (11)$$

for $343 \leq T \leq 2487$ K.⁵ Eqs. (10) and (11) agree within a few percent with all studies except that of Marshall and Fontijn.¹⁵ Rate constants for the reverse reactions can be calculated from JANAF equilibrium constant values,¹¹ and the values for both forward and reverse rate constants are compiled in Table I.

$H + H_2O \rightarrow H_2 + OH$ and $D + D_2O \rightarrow D_2 + OD$: There are only two direct studies of reaction (3), one being with the FP-ST¹⁹ and the other being with the LP-ST⁸ techniques. The results from these two studies are given in Arrhenius form as,

$$k_3 = (4.58 \pm 0.61) \times 10^{-10} \exp(-11558 \pm 243 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (12)$$

for $1246 \leq T \leq 2297$ K, and,

$$k_3 = (3.99 \pm 0.42) \times 10^{-10} \exp(-10750 \pm 500 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (13)$$

for $1600 \leq T \leq 2500$ K, respectively. These two equations agree within combined error limits over the range of T overlap. At high T, there is only one direct FP-ST study²⁰ of reaction (3D). These results are described for $1285 \leq T \leq 2261$ K by the Arrhenius expression.

$$k_{3D} = (2.90 \pm 0.73) \times 10^{-10} \exp(-10815 \pm 356 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (14)$$

There are numerous earlier studies²¹⁻²⁵ of reaction (-3) with four being particularly notable.^{21,23-25} JANAF equilibrium constants¹¹ have been used to transform these reverse rate constant data²⁵ to those for the forward process, and an evaluation has been carried out for $250 \leq T \leq 2581$ K. A three parameter expression describes the results.

$$k_3 = 1.56 \times 10^{-15} T^{1.52} \exp(-9249 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (15)$$

Since the data are not as extensive, an extended expression for k_{3D} cannot be evaluated; however, values for the back reaction (-3D) can be derived from JANAF values.¹¹ This expression and the other derived expressions are given in Table I.

$O + H_2O \rightarrow OH + OH$ and theory for $O + D_2O \rightarrow OD + OD$: There are three direct studies of reaction (4)²⁶⁻²⁸ for the T-ranges, 1053-2033 K,²⁶ 1500-2500 K,²⁷ and 753-1045 K,²⁸ respectively. The FP-ST results from Sutherland, et al.²⁶ can be represented by the Arrhenius equation,

$$k_4 = 1.10 \times 10^{-10} \exp(-9929 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (16)$$

for $1288 \leq T \leq 2033$ K. The results from Lifshitz and Michael²⁷ are,

$$k_4 = (1.12 \pm 0.20) \times 10^{-10} \exp(-9115 \pm 304 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (17)$$

for $1500 \leq T \leq 2500$ K. The activation energies are different with the latter being lower than the former by ~10%. Evenso, the agreement between the two studies is good with eq. (16) being ~30-40% lower than that of eq. (17). The spread in the data from each study is ~±15-20%, and the two sets overlap over the common T-range. Sutherland, et al.²⁶ have also carried out Flash Photolysis-Resonance Fluorescence (FP-RF) studies at lower T, 1053 to 1123 K, and these data are the most accurate to date for reaction (4). There are numerous experimental studies of the back reaction (-4).^{22b,29} These data have been combined with that from the two FP-ST studies through the JANAF equilibrium constants¹¹, and a comparison between the combined database for reactions (4) and (-4) with theoretical calculations has been made.⁷ The theoretical result,

$$k_4^{\text{th}} = 7.48 \times 10^{-20} T^{2.70} \exp(-7323 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (18)$$

agrees with experiment within experimental error over the T-range, 700-2500 K. There are no data for the $O + D_2O$ reaction. Therefore, a theoretical estimate that is consistent with the successful protonated case, eq. (18),⁷ can be used as a starting point in experiment design and/or in chemical modeling experiments for the D_2/O_2 system. The calculated result for $700 \leq T \leq 2500$ K is,

$$k_{4D}^{\text{th}} = 2.05 \times 10^{-19} T^{2.56} \exp(-8286 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (19)$$

These expressions and the transformed reverse rate constant values are listed in Table I.

$H + O_2 + M \rightarrow HO_2 + M$: FP-ST results have been obtained for this reaction.¹⁰ The third-order rate constant has been determined for $746 \leq T \leq 987$ K to be $k_5 = (7.1 \pm 1.9) \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ with Ar as the heat bath gas.¹⁰ The Baulch et al.³⁰ recommendation is,

$$k_{H+O_2+Ar} = 4.1 \times 10^{-33} \exp(+500 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}. \quad (20)$$

A recent flow tube study³¹ for $298 \leq T \leq 639$ K in He gives,

$$k_{H+O_2+He} = (4.0 \pm 1.2) \times 10^{-33} \exp(+560 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}. \quad (21)$$

Since He and Ar have about the same effective collision efficiency, the FP-ST result can be compared to both eqs. (20) and (21). At the mean temperature, $T = 850$ K, eqs. (20) and (21) give respective values of 7.4×10^{-33} and 7.7×10^{-33} to be compared to the FP-ST result of $7.1 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. These results combine to give excellent agreement for the recombination reaction over the

temperature range, 300 to ~1000 K. Since the Hsu et al.³¹ result is the most direct to date, it is listed in Table I. Similar experiments for $D + O_2 + M$ have not been reported, but eq. (21) can be used in D_2/O_2 modeling calculations as a first estimate.

CONCLUSION

The most important rate constants in the branching chain oxidations of H_2 and D_2 have now been measured by the direct flash and/or laser photolysis-shock (FP- or LP-ST) tube technique. The only exceptions are the $O + D_2O$ and $D + O_2 + M$ reactions. There are of course several other reactions of secondary importance that must be included in complete oxidation mechanisms, and these have been considered in most earlier studies. The importance of these reactions increases as the extent of reaction increases, and, in the large conversion H_2/O_2 studies where OH-radicals are observed throughout the entire course of the reaction, the relative effects of these secondary reactions are greater than in the small conversion studies where the initial stages of the reaction are only monitored. However, even in the high conversion studies, the five reactions considered here and their reverses, always exhibit higher sensitivity than all other reactions in sensitivity analysis calculations. It can therefore be concluded with these new direct FP- and LP-ST data that the main features of the oxidation mechanisms are now substantially solved.

The evaluated rate constants are given in Table I along with comments regarding accuracy and the T-range of applicability. We recommend that these rate constants be used as initial starting values in oxidation studies. To be sure, the rate constants are known only within certain error limits, and therefore, any adjustments within these error limits are certainly allowed. However, if a particular observation implies the use of rate constants that are substantially outside the bounds set by these direct studies, then an inconsistency exists. In this event, new explanations must be found, and this may imply modifications in the reaction rate constants for initiation and/or perhaps in secondary chemical processes.

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Table I: Recommended $k = A T^n \exp(-B/T)$ expressions for the H_2/O_2 and D_2/O_2 Reactions from the FP- or LP-ST Studies.

Reaction	$A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	n	B/K	Comments and Reference
Protonated reactions:				
$H + O_2$	$1.15(-10)^a$	0	-6917	1100 - 2050K, $\pm 27\%$ ⁹
$OH + O$	$8.75(-12)$	0	1121	1100 - 2050K, $\pm 27\%$ ^{9,11}
$O + H_2$	$8.44(-20)$	2.67	-3167	297 - 2495K, $\pm 30\%$ ¹²
$OH + H$	$3.78(-20)$	2.67	-2226	297 - 2495K, $\pm 30\%$ ^{11,12}
$H + H_2O$	$1.56(-15)$	1.52	-9249	250 - 2297K, $\sim \pm 25\%$ ^{11,25}
$OH + H_2$	$3.56(-16)$	1.52	-7513	250 - 2581K, $\sim \pm 25\%$ ²⁵
$O + H_2O$	$7.48(-20)$	2.70	-7323	700 - 2500K, $\sim \pm 50\%$, theory ⁷
$OH + OH$	$7.19(-21)$	2.70	1251	700 - 2500K, $\sim \pm 50\%$, theory ⁷
$H + O_2 + M$	$4.0(-33)^b$	0	560	298 - ~ 1000 K, $\sim \pm 30\%$ ³¹
Deuterated reactions:				
$D + O_2$	$1.09(-10)$	0	-6937	$1050 \leq T \leq 2300$ K, $\pm 27\%$ ⁹
$OD + O$	$9.73(-12)$	0	526	$1050 \leq T \leq 2300$ K, $\pm 27\%$ ^{9,11}
$O + D_2$	$2.43(-16)$	1.70	-4911	$343 \leq T \leq 2487$ K, $\pm 16\%$ ⁵
$OD + D$	$1.04(-16)$	1.70	-3806	$343 \leq T \leq 2487$ K, $\pm 16\%$ ^{5,11}
$D + D_2O$	$2.90(-10)$	0	-10815	$1285 \leq T \leq 2261$ K, $\pm 27\%$ ²⁰
$OD + D_2$	$6.56(-11)$	0	-3320	$1285 \leq T \leq 2261$ K, $\pm 27\%$ ^{11,20}
$O + D_2O$	$2.05(-19)$	2.56	-8286	> 700 K, theory ⁷
$OD + OD$	$1.85(-20)$	2.56	452	> 700 K, theory ⁷

^aparentheses denotes the power of ten; i. e., 1.15×10^{-10} . ^bunits are $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

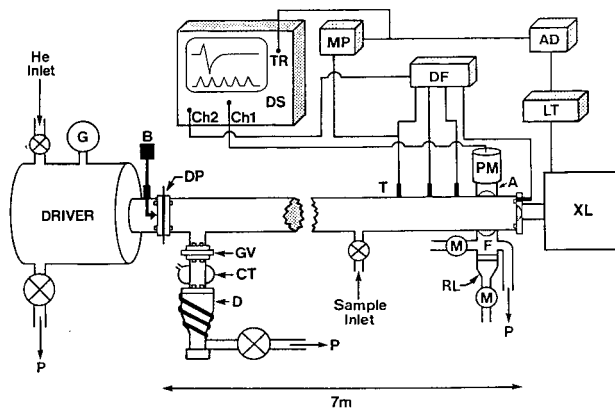


Fig. 1: Schematic diagram of the apparatus. P - rotary pump. D - oil diffusion pump. CT - liquid nitrogen baffle. GV - gate valve. G - bourdon gauge. B - breaker. DP - diaphragm. T - pressure transducers. M - microwave power supply. F - atomic filter. RL - resonance lamp. A - gas and crystal window filter. PM - photomultiplier. DS - digital oscilloscope. MP - master pulse generator. TR - trigger pulse. DF - differentiator. AD - delayed pulse generator. LT - laser trigger. XL - excimer laser.

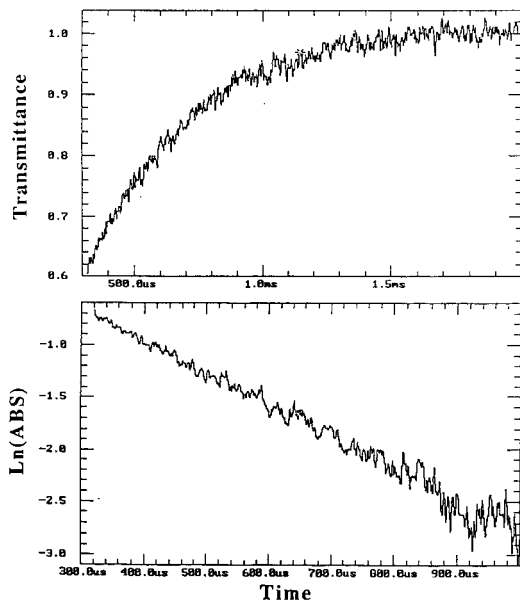


Fig. 2: Top: H-atom transmittance as a function of time after laser photolysis in the reflected shock wave region. Bottom: First-order plot of $\ln[\text{ABS}]_t$ against time that is obtained from the top record.